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**AFOSR-87-0251. HIGH TEMPERATURE PROPERTIES OF CERAMIC/CARBON SYSTEMS
IN AN OXIDIZING ENVIRONMENT.**

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Technical Report for One-Year Period (June 1, 1987 - May 31, 1988)

A. SUMMARY

The object of our research is to identify and learn to constructively modify the features of the bonding interactions that lead to brittleness in carbon-based ceramic materials. We have been examining the titanium/carbon and tungsten/carbon systems, both the naturally occurring carbides and artificially constructed superlattices. We are examining the question of whether artificially constructed multilayer (superlattice) structures offer an advantage over the naturally occurring crystalline structures in maintaining high temperature mechanical stability in an oxygen-containing environment. This is related to the modification of the type of bonding, metallic versus covalent, possible by making artificial structures and how this affects brittleness and hence fracture behavior.

In the first year of the study (June 1, 1987 - May 31, 1988) experimentally we have concentrated on the fabrication and characterization of titanium-carbon and tungsten-carbon superlattices and especially on the behavior at the metal-carbon interface. Theoretically we have examined the relationship of mechanical stability to the amount of covalent versus metallic bonding, how changes in this bonding lead to structural

instability, and how the type of bonding and elastic behavior can be altered by fabricating superlattice structures. In the theoretical as in the experimental component, we have especially focussed on the behavior at the metal-carbon interface for the superlattice structures. The theory and experiment are in agreement that for the titanium-carbon superlattices, the interface has a graphite-like carbon atomic arrangement rather than a carbide-like arrangement. Thus the interface most likely consists of simply a layer of graphite adjoining a titanium surface, i.e., not a strongly bonded interface. On the other hand, our experimental results at present indicate carbide-like interface behavior for the tungsten-carbon system, and we are going on theoretically to examine this question in our total energy computations modeling the interface behavior.

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B. THEORETICAL COMPONENT OF RESEARCH

Our theoretical work is based on the use of full-potential all-electron total energy calculations to predict stable and metastable crystallographic states of complex material systems. Full potential calculations allow for a completely general spatial variation of electronic charge, i.e., no artificial charge shaping constraints are imposed on the electronic system. Our total energy calculations have utilized our recently developed self-consistent linear combination of muffin-tin orbitals (LMTO) electronic structure method. This is a full-potential, all-electron, variation on standard LMTO electronic structure methods and, along with careful self-consistent determination of the parameters involved, allows accurate total energy calculations for the type of low symmetry systems involved in this study.

We have used total energy calculations to predict crystal structures of naturally-occurring materials for titanium carbide and tungsten carbide, and to recognize the role of competition between covalent and metallic bonding in determining these structures. We have used total energy calculations to study the stabilization of superlattices. We have already completed extensive computer modeling computations for the titanium/carbon system and have initiated corresponding studies on the tungsten/carbon system. Particular emphasis has been placed on the behavior at the metal-carbon interface in the superlattices. The crucial question is whether the carbon bonds carbidically with the metal or just lays passively graphitically next to the metal. This is pertinent to both diffusion of carbon into metal and stability

of the superlattice. An important question is whether there is a difference between titanium and tungsten in this regard.

For TiC, the crystal structure is dominantly determined by the system's seeking to achieve the optimal carbon p-with-titanium d covalent bonding. This occurs for the NaCl-type cubic structure, as is illustrated by δ -projected density of states calculations we have performed. Our total energy calculations yield a minimum energy (stable configuration) for a lattice constant very close to experiment and with cohesive energy and elastic constants in good agreement with experiment (see Table I attached). Detailed computer modeling allows us to understand why this structure is preferred to the hexagonal structure as occurs for WC. For tungsten there are two additional d electrons compared to titanium. This provides additional opportunity for metallic bonding, and our calculations predict the change to a hexagonal structure in close agreement with experiment. Furthermore the energy difference to the very high temperature NaCl-type phase of WC is also found in close agreement with experiment. (Theory gives 3018K, while the experimental transition is at 3028K.)

We have focussed on the titanium-carbon interface through use of a model 2×2 Ti_2C_2 superlattice structure (see Fig. 1). By studying the total energy as a function of the distance parameter d_1 , giving the separation between the titanium and carbon layers, as shown in Figure 2, we can see whether the carbon will bind carbidically to the tungsten or whether graphitic binding to other carbons will dominate the interface structural behavior and binding. At a certain d_1 value the interface has carbidic structure. As d_1 is increased, the carbon separates from Ti to

form graphite. As d_1 is varied, the choice between these structures is essentially determined by the competition between Ti-C bonds and C-C bonds at the superlattice interface. As can be seen from Figure 2, at the carbidic end (low d_1), energy considerations favor the carbon being bound even more tightly to Ti than in TiC. However, this is outweighed by the fact that the graphite structure has lower energy. In fact, the minimum of energy is predicted for a "corrugated graphite" configuration. Thus we conclude that the titanium-carbon superlattice interface consists of a graphite layer adjoining the metal surface. This agrees with the experimental observations discussed in the next section, and implies a relatively weakly cohesive superlattice structure. We are now going on to the corresponding modeling for tungsten, and it will be interesting to see what the increase in number of metallic electrons does to the interface structure and binding.

C. EXPERIMENTAL COMPONENT OF RESEARCH

We performed a complete study of the properties of the carbon-metal interface using Electron Energy Loss Spectroscopy (EELS), Auger spectroscopy (AS), X-ray diffraction, Rutherford backscattering (RBS) and nuclear elastic scattering with protons and alpha particles. The latter techniques were employed to determine the presence of oxygen impurities in the samples. The structural stability of the superlattices of carbon-metal were investigated over a wide range of temperatures. The summary of the Ti/C measurements is given in the first part of this section and the second part deals with the most recent measurements in the W/C system.

Ti/C:

We studied a series of superlattices of variable composition. From 4.7Å carbon thickness to 41Å, the metal layer thickness was varied from 20Å to about 38Å. X-ray diffraction and microcleavage transmission electron microscopy were employed to characterize the bulk and layers thicknesses. We employed EELS to study the sample composition as a function of depth. We used standard samples to identify the different energy loss peaks. The oxidation state of titanium was identified by measuring the 3p core ionization losses, which are extremely sensitive to oxygen bonding. We would like to point out that EELS is a more chemically sensitive technique than AS. If one combines mild sputtering conditions (very low ion currents and short times), the depth analysis capabilities of EELS can be significantly extended. The nuclear scattering techniques were employed to determine the presence of

impurities in the sample and to check the distribution of the elements in the layers. In order to detect the presence of oxygen in the bulk, we used the elastic scattering resonance of alpha particles at 3.05 Mev. For all the samples we observed the presence of oxygen in the bulk. The AS and EELS studies show the presence of graphitic carbon and of titanium oxide. We determined from our measurements that TiO_2 is formed at the interface between Ti and C. We did not observe the presence of any significant metal-carbon bond; carbides were totally absent from all the samples investigated. The titanium layers have a bulk metal character, the carbon layers are graphitic. Such multilayers retain their structures at high temperatures, but can be susceptible to "peeling off" effect, destroying the structural integrity of the material.

W/C:

A series of samples with carbon thickness between 4 and 10A was investigated over a wide range of temperatures. The metal thicknesses were between 6 and 15A, and the average number of layers was around 200. The samples were studied using AS, EELS, RBS, nuclear elastic scattering, and Surface Electron Energy Loss Fine Structure (SEELFS). The latter technique was employed to determine the short range crystallographic order around the carbon atom. The measurements were performed between room temperature (RT) and 1300K.

By contrast with the Ti/C samples, no evidence of oxide formation was found in the bulk of the samples. The only oxygen we detected was from simple surface contamination by exposure to air

(a fraction of a monolayer). The EELS as a function of energy indicated the presence of a carbide in the sample. In order to identify the carbide we employed the SEELFS technique. We studied the carbon K-edge using a primary electron beam energy of 2500 eV. The data was collected on line using an IBM personal computer PS2/50. The data was processed off line using an EXAFS analysis package developed by us for use at NSLS (National Synchrotron Light Source). An example of a typical Fourier transform spectrum (magnitude) is shown in Figure 3. The spectrum is characteristic of tungsten carbide; the given example is at 900K. We observed that the amount of carbide increases with temperature; this was observed by the enhancement of the carbide SEELFS signal. We observed a similar effect in our EELS measurements, where significant variations in the spectra were observed as function of temperature for all the samples. Figures 4 and 5 are illustrations of such changes. The EELS spectra were collected with a primary beam of 600 eV; we can clearly observe that the spectrum at 1100K is different from that of the 700K measurements. The changes in the peaks are related to variations in the interfaces W-C, indicating an increase in the interface thickness. From EELS studies at different primary energies (100 to 2300 eV) and the SEELFS results we inferred that the carbide is formed at the interface and that the interface region increases with temperature. We did not observe any oxide formation and the material shows a high degree of structural integrity. From the point of view of the multilayer spacings there should be significant variations, something that needs to be considered when using W/C superlattices as optical devices. We plan to determine the thickness of the interface as a

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function of temperature and to react the surface with oxygen at high T. We are planning to extend our temperature range to 2000K and to start measurements on the elastic properties of this novel W/C structure.

FIGURES: The sample shown in the figures has a carbon thickness of 7A and a tungsten thickness of 7A, and 200 layers per element.

Figure 3. Magnitude of the Fourier transform of a W/C superlattice at 900K.

Figure 4. EELS of a W/C sample at 700K, primary energy 600 eV.

Figure 5. EELS of a W/C sample at 1100K, primary energy of 600 eV.

D. PUBLICATIONS AND PRESENTATIONS

Publications

1. "Interface Structure and Stability in Ti/C Superlattices", to appear in Materials Research Society Proceedings (1988).
2. "Total Energies and Bonding for Crystallographic Structures in Titanium Carbon and Tungsten Carbon Systems", to appear in Physical Review B (1988).

Presentations

1. "Full Potential LMTO Calculations of Interface Energies in Titanium-Carbon Systems", American Physical Society Meeting, New Orleans, March, 1988.
2. "Oxygen Effects in Ti/C Multilayers", American Physical Society Meeting, New Orleans, March, 1988.
3. "Interface Structure and Stability in Ti/C Superlattices", Materials Research Society Meeting, Reno, April, 1988.

TABLE I. Summary of calculated parameters of each system, with comparisons to experiment where available.

System	Lattice constants (a.u.)	Cohesive energy (eV/atom)	Elastic constants*	DOS at E_f (states/Ry)
TiC (NaCl)	8.18	8.89	$B = 2.14$	3.16
exp:	8.182	7.04	$B = 2.42$	
WC (NaCl)	8.10	9.46	$B = 3.21$	14.53
exp:	8.02			
TiC (Hex.)	$a = 5.84$ $c = 5.02$	8.11	$B = 2.31$ $Y_s = 3.18$ $\sigma_{xx} = 0.387$	2.17
WC (Hex.)	$a = 5.44$ $c = 5.33$	9.72	$B = 3.29$ $Y_s = 8.48$ $\sigma_{xx} = 0.121$	3.23
exp:	$a = 5.492$ $c = 5.361$	8.34	$B = 3.31$	
Ti ₂ C	$c = 9.17$	8.03	$\partial^2 E / \partial^2 c = 0.76$ (Ry/a.u. ²)	25.99
Ti ₂ C ₂				
$d_3 = 4.50$		4.80		37.33
$d_3 = 1.83$		6.92		68.65

* B = Bulk modulus (Mbar), Y_s = Young's modulus (Mbar), σ_{xx} = Poisson's ratio

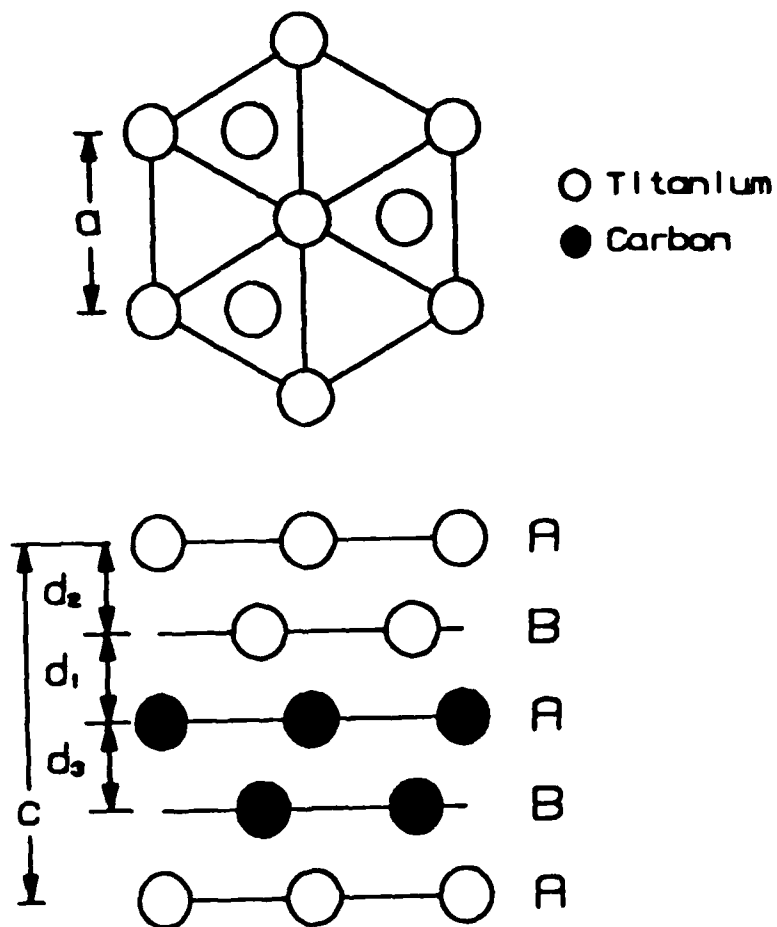
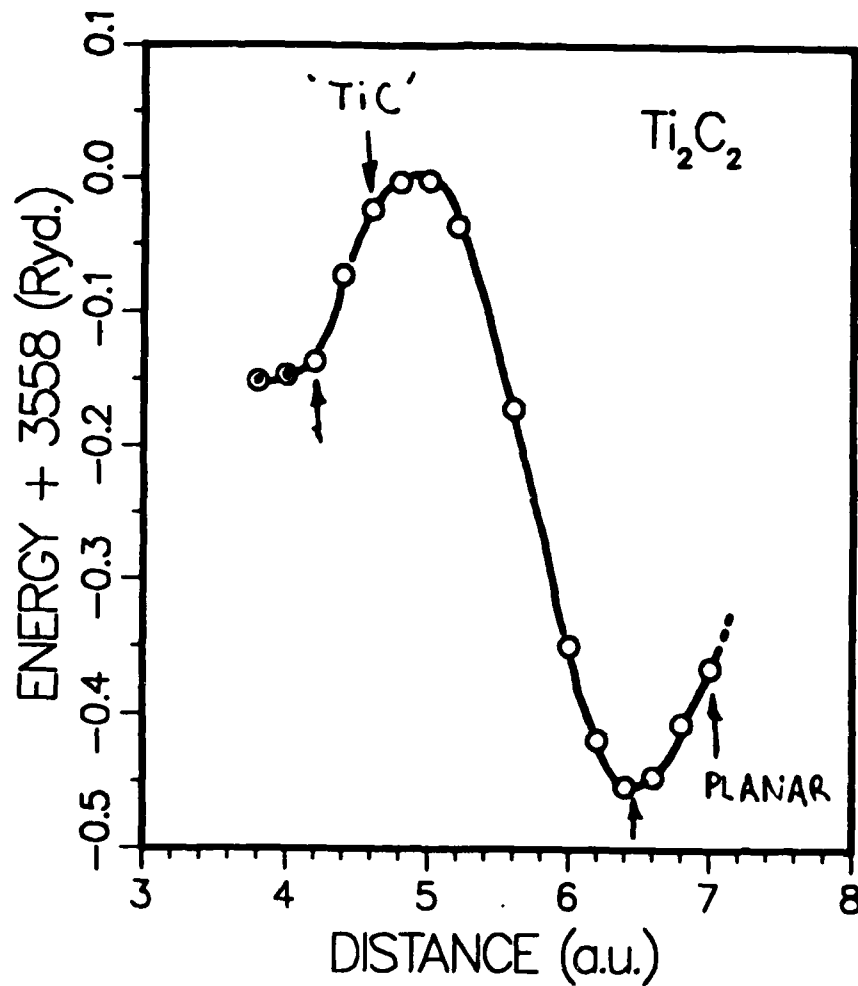


Fig. 1

Ti_2C_2 ENERGY v.s. D_1



- AT 'CARBIDE END' CARBON \bullet BOUND MORE TIGHTLY TO Ti THAN IN TiC
- GRAPHITE STRUCTURE LOWER IN ENERGY
- MINIMUM AT 'CORRUGATED GRAPHITE' (residual interaction with Ti)
- REDUCE GRAPHITE LATTICE, GET $\sim .15 \text{ Ryd/ATOM}$

Fig. 2

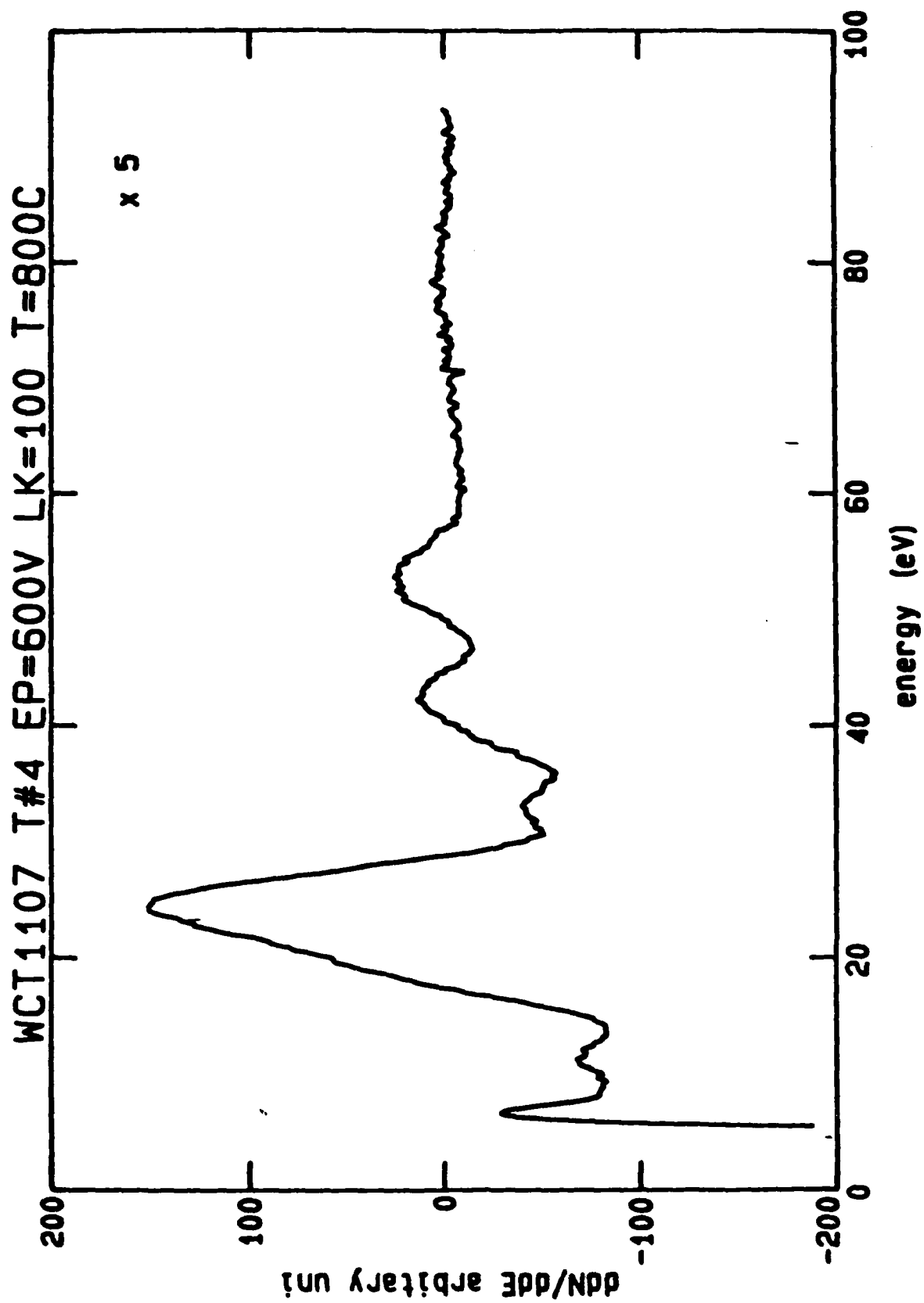


Fig. 3

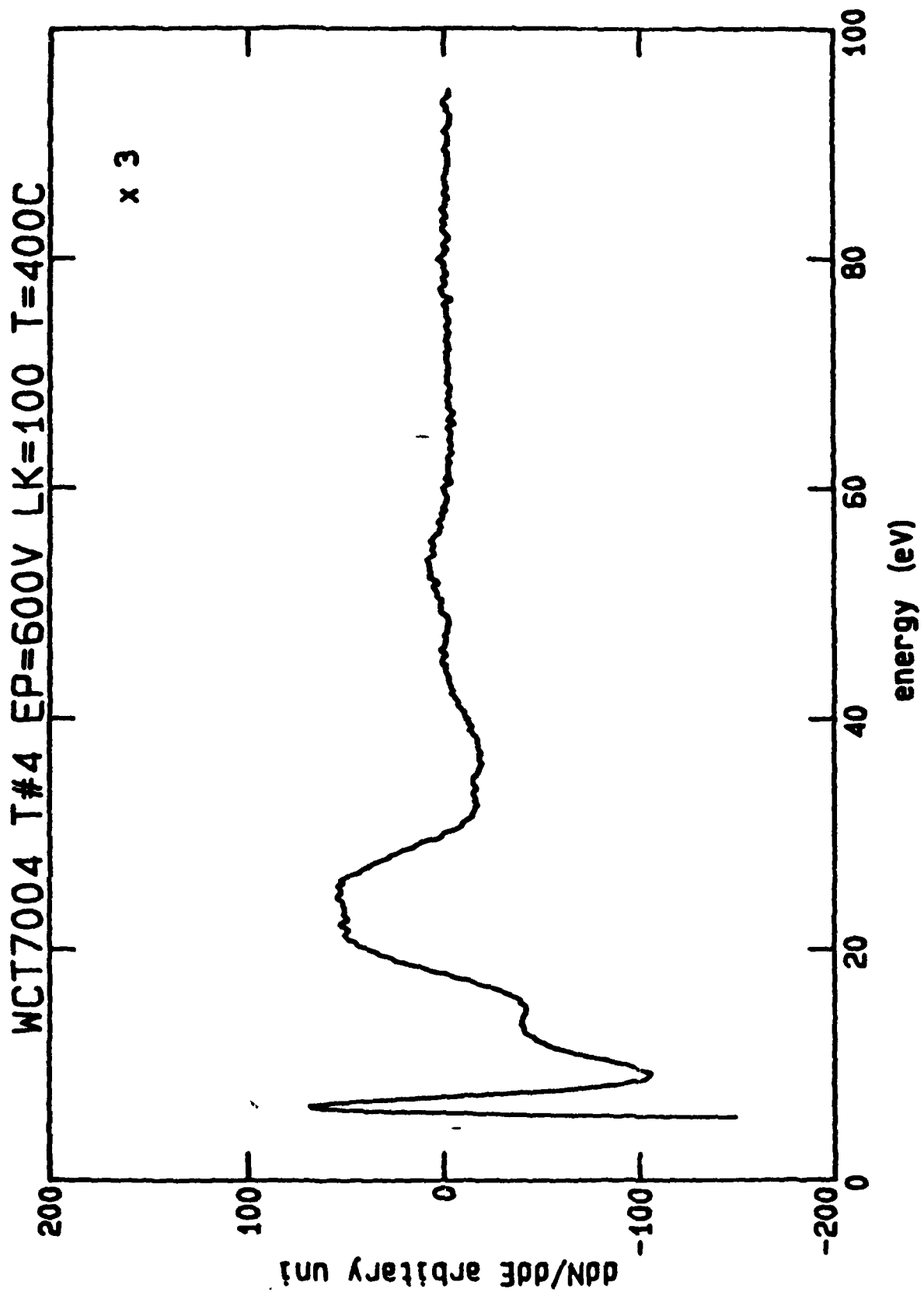
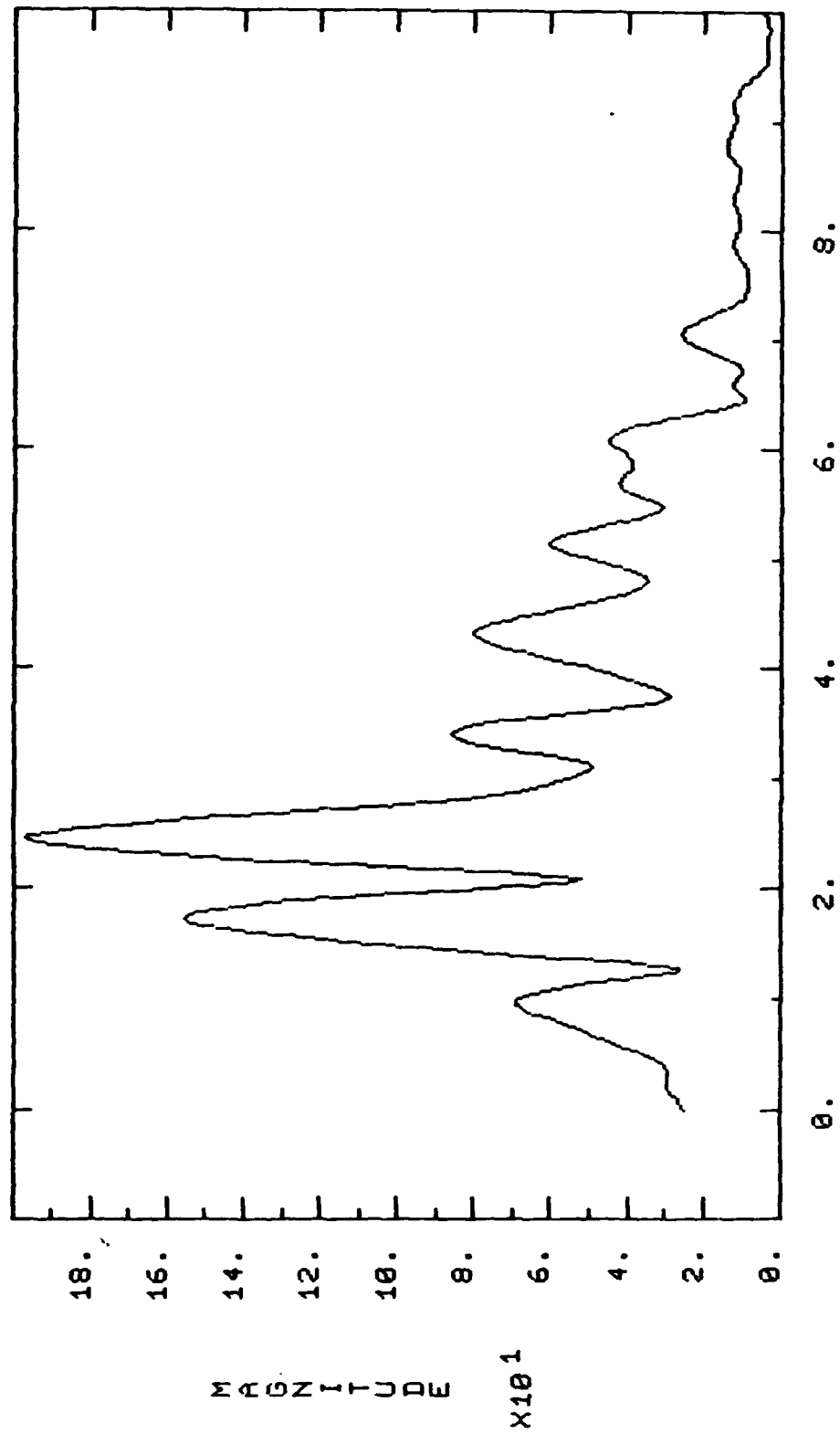


Fig. 4



R A D I U S

\EXAPLT\DAT\B600C.DAT 2/6 05-14-1988FT OF K#1 OVER 4096 PTS FROM 1.6 TO 9.5 K

Fig. 5